# THE CATALYTIC HYDROGENATION OF QUINOLINES AT HIGH PRESSURES

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# THE CATALYTIC HYDROGENATION OF QUINOLINES AT HIGH PRESSURES

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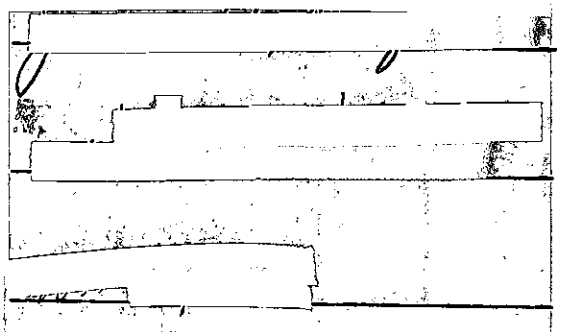

Date Approved by Chairman June 4, 1951

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ABSTRACT

A study has been made of the high pressure catalytic hydrogenation of quinoline and methyl-substituted quinolines, using Adams' platinum oxide catalyst in glacial acetic acid. A high pressure micro shaking mechanism equipped with a heating jacket was employed at pressures ranging from 1000 to 2000 p.s.i. and from 20 to 70 °C. Glass liners were invariably used to avoid contamination. The total volume of the system including the liner, was approximately 40 ml.

The rate of hydrogenation is first order in hydrogen pressure, zero order in hydrogen acceptor and directly proportional to the amount of catalyst.

Quinoline, as well as 6-methylquinoline, 7-methylquinoline and 8-methylquinoline, hydrogenates to 1,2,3,4-tetrahydroquinoline; however, decahydroquinoline begins to form before all the quinoline is converted to the tetrahydro derivative.

With 2-methylquinoline, 3-methylquinoline and 4-methylquinoline the results are quite different. A 5,6,7,8-tetrahydro product forms simultaneously with the 1,2,3,4-tetrahydro compound. Evidence is presented that suggests the former compounds hydrogenate to the decahydroquinolines much faster than the latter compounds do. Runs stopped at 40 per cent hydrogenation yielded the following per cent of 1,2,3,4-tetrahydro and 5,6,7,8-tetrahydro derivatives, respectively: 2-methylquinoline, 74-6; 3-methylquinoline, 95-1.2 and 4-methylquinoline, 64-14.

The relative rates of hydrogenation to the 1,2,3,4-tetrahydro and to the decahydro derivatives, respectively, are: quinoline, 1.00, 1.00; 2-methylquinoline, 0.94, 1.31; 3-methylquinoline, 1.40, 1.70;

4-methylquinoline, 0.05, 0.08, 1.26 (hydrogenation of 5,6,7,8-tetrahydro-4-methylquinoline to the decahydro analogue); 6-methylquinoline, 0.87, 0.90; 7-methylquinoline, 0.93, 0.63; and 8-methylquinoline, 1.21, 0.20.

The energies of activation for the reduction of the pyridine ring of these quinolines range from 3,700 to 6,400 calories per mole; for the benzene ring, 7,200 to 12,000 calories per mole.

Increasing the hydrogen pressure from 1000 to 2000 p.s.i. slightly increases the rate of hydrogenation to the tetrahydroquinolines but decreases the rate of hydrogenation to the decahydro derivatives. The rate varies similarly with increasing amounts of hydrogen acceptor. Both steps of the hydrogenation increase with increasing amounts of catalyst.

# THE CATALYTIC HYDROGENATION OF QUINOLINES AT HIGH PRESSURES

## I. INTRODUCTION

Catalytic hydrogenation has long been an important process in industry and laboratory synthesis, as is evidenced by the many papers dealing with all phases of the subject.

Although the topic of optimum conditions, catalyst, pressure, temperature, etc., has continually been a problem, it was not until 1945, when H.A. Smith, et al, published the first three of a series of papers on catalytic hydrogenation, that a systematic kinetic study was reported. These workers investigated the kinetics of hydrogenation of phenyl-substituted aliphatic acids[1], benzene and its homologues[2], methyl-substituted benzoic acids[3], and cyclohexenes and cyclohexadienes[4]. Using Adams' platimum catalyst[5] in glacial acetic acid at an initial hydrogen pressure of 64 p.s.i. they concluded that the reaction rate is first order with respect to hydrogen pressure, zero order with respect to hydrogen acceptor

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[1]H.A. Smith, D.M. Alderman, Jr. and F.W. Nadig, J. Am. Chem. Soc., 67, 272 (1945).

[2]H.A. Smith and E.F.H. Pennekamp, J. Am. Chem. Soc., 67, 276, 279 (1945).

[3]H.A. Smith and J.A. Stanfield, J. Am. Chem. Soc., 71, 81 (1949).

[4]H.A. Smith, D.M. Alderman, Jr., C.D. Shacklett and C.M. Welch, J. Am. Chem. Soc., 71, 3772 (1949).

[5]R. Adams, V. Voorhees and R.L. Shriner, Organic Synthesis, Coll. Vol. I (New York, John Wiley and Sons, Inc., 1932), p. 463.

and directly proportional to the amount of catalyst used. In addition, the phenyl group is strongly adsorbed on the catalyst while other portions are not and the resonance does not greatly effect the rate. Finally, the more symmetrically substituted a molecule, the faster the rate.

This investigation has also been extended to the pyridine nucleus with quite similar results[6]; however, some additional observations were made. First, the rate of hydrogenation decreased slightly with increasing concentration of pyridine. Second, the ease of hydrogenation of methylpyridines in decreasing order is alpha, beta and gamma. Finally, the energy of activation was not constant over the range 15 to 45 °C.

Trimble[7] and Hecht[8] of these laboratories have made an even more interesting step by studying the kinetics of hydrogenation of quinoline and methylquinolines. They also used Adams' catalyst in glacial acetic acid. Quinoline hydrogenates to the 1,2,3,4-tetrahydroquinoline, but more slowly to decahydroquinoline. These workers present evidence that the latter compound begins to form before all the quinoline is hydrogenated to the tetrahydro derivative. Both steps of hydrogenation were found to be first order in hydrogen, zero order in hydrogen acceptor and directly proportional to the amount of catalyst. In addition, they determined the effect of methyl substitution on the rate of

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[6]J. A. Stanfield, "The Kinetics of Catalytic Hydrogenation," Doctoral Dissertation, University of Tennessee, 1947.

[7]A. T. Trimble, Jr., "The Catalytic Hydrogenation of Quinoline," Master's Thesis, Georgia Institute of Technology, 1949.

[8]J. L. Hecht, "The Catalytic Hydrogenation of Quinolines," Master's Thesis, Georgia Institute of Technology, 1950.

hydrogenation and the activation energies of the pyridine ring, 5,800 calories per mole, and the benzene ring, 10,000 calories per mole.

R.H. Baker and R.D. Schuetz[9] have recently extended the use of Adams' platinum catalyst to high pressures. They have successfully reduced some simple aromatic compounds on a preparative scale in a matter of minutes, where the reactions at low pressures required hours. The first order dependence on hydrogen pressure and zero order dependence on acceptor is also true at high pressures. However, the ratio of rates at low and high pressures for two different compounds was not the same.

The present investigation has as its purpose an extention of the work of Trimble and Hecht on quinolines using the high pressure method of Schuetz and Baker. The method of attack is to study the kinetics of hydrogenation of the quinolines at high pressures using Adams' catalyst in glacial acetic acid. Various factors which influence the rate are to be determined and, in addition, comparisons with the results at low pressures are to be made. No such study has previously been attempted.

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[9]R.H. Baker and R.D. Schuetz, J. Am. Chem. Soc., 69, 1250 (1947).

# II. THEORETICAL

Through chemical kinetics the rates of reactions and various factors influencing the rates may be studied. Although most inorganic reactions take place at rates too rapid to measure, many organic reactions may be conveniently studied by kinetics. Every chemical reaction proceeds at a definite rate depending upon the conditions, such as concentration, temperature, catalyst, etc. It is convenient to study the effect of these conditions in terms of the reaction rate constant.

## A. The Reaction Rate

From a quantitative standpoint, it is useful to define the "order of reaction." This is the number of atoms or molecules whose concentrations determine the rate of the reaction.

Consider the reaction:

$$xA + yB = C. \tag{1}$$

If the volume is constant, then the rate of disappearance of A, $-\frac{dc}{dt}$, is:

$$-\frac{dc}{dt} = k\,(A)^x\,(B)^y, \tag{2}$$

where c is the concentration of A, t is the time in minutes and k is defined as the reaction rate constant, or merely the rate constant.

The exponents x and y are the orders of reaction with respect to the reacting substances A and B, respectively. The sum of x and y is the total order of the reaction. There are various experimental methods of determining these values, but it will not be necessary to

discuss them here.

In the present work it was necessary to consider only a first order reaction, where in equation (2) we may neglect B and let x equal to one. Then if c equals the concentration of A:

$$-\frac{dc}{dt} = kc \ . \tag{3}$$

Integration of equation (3) and convertion to common logarithms gives:

$$\log \frac{c_1}{c_2} = \frac{k(t_2 - t_1)}{2.303} \ . \tag{4}$$

Equation (4) may be simplified by replacing $c_1$ by $c_o$, the initial concentration; $c_2$ by c, the concentration at time t; and $t_1$ by 0. This gives:

$$\log \frac{c_o}{c} = \frac{kt}{2.303} \ . \tag{5}$$

Since the concentration of a gas is proportional to its pressure, the first order equation becomes:

$$\log \frac{p_o}{p} = \frac{kt}{2.303} \ . \tag{6}$$

It should be emphasized that equation (6) is in error. If it is to be valid, the system must obey Henry's Law, i.e., the fugacity of the hydrogen must be proportional to the mole fraction of the hydrogen dissolved in the liquid phase. It is permissible to replace the concentration of hydrogen by the mole fraction since its solubility is low. However, at hydrogen pressures of approximately 1000 p.s.i., the fu-

gacity is not equal to the pressure; the error is approximately 6 per cent. A more exact equation would result if $p_o/p$ in equation (6) was replaced by $p_o \gamma_o / p \gamma$, where $\gamma$ is the activity coefficient of the hydrogen gas. However, in this work the pressure drop for most runs was only about 400 p.s.i. The result is that the ratio of the activity coefficients ($\gamma_o / \gamma$) is not much greater than one and the error in neglecting this ratio in the rate expression is within experimental error. The error is greater as the ratio of $p_o/p$ becomes larger, i.e., as the pressure drop increases.

According to equation (6), a plot of log $p_o/p$ against t will give a straight line of slope k/2.303. If the rate constant, k, determined by this method is divided by the grams of catalyst used, the rate is independent of catalyst concentration. The units of k are therefore reciprocal minutes per gram.

## B. Factors Influencing the Rate Constant

### 1. Temperature.

The most convenient method of expressing the change in the reaction rate with temperature is given by the classical Arrhenius equation:

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}, \qquad (7)$$

where k is the rate constant, T is the absolute temperature, R is the universal gas constant, and $E_a$ is the energy of activation for the reaction.

Integration of equation (7) gives:

$$\ln k = - \frac{E_a}{RT} + \ln PZ^o , \qquad (8)$$

where the constant of integration is equal to ln $PZ^o$; P is an empirical probability factor and $Z^o$ is the collision frequency. Quite often this term is altered by substitution or change in catalyst.

If $E_a$ is constant over a given temperature range, a plot of ln k against 1/T will give a straight line. Frequently a more useful equation is another integrated form of equation (7):

$$\log \frac{k_2}{k_1} = - \frac{E_a}{2.303R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) . \qquad (9)$$

Once the energy of activation is known, we may determine the rate constant at any other temperature within the range where the energy of activation is constant. However, in this work it was convenient to use equation (9) to correct rate constants to some standard temperature.

2. Volume of the Gas.

Smith and Fuzek[1] have recently pointed out that all too frequently observers fail to report the volume of the vapor phase in hydrogenation. They showed that the rate constant is inversely proportional to the volume; consequently, if rate constants are to be comparable, they should be multiplied by the volume factor. All rate constants reported in this thesis have been multiplied by the volume of the hydrogen void and the units are ml. $min.^{-1}$ $gram^{-1}$.

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[1]H.A. Smith and J.F. Fuzek, J. Am. Chem. Soc., 70, 3743 (1948).

3. Solvent.

In many kinetic reactions the solvent is of prime importance, and this has been found to be the case in catalytic hydrogenation.

Using Adams' platinum catalyst in acetic acid, Overhoff and Wibaut[2] hydrogenated quinoline to trans-decahydroquinoline; in $C_2H_5OH$-HCl solution the cis and trans isomers were isolated. They also found that the ratio of the rates for two substituted pyridines was not constant in the two solvents mentioned above.

Foresti[3] studied the hydrogenation of benzene and some of its homologues using a platinum catalyst and reported the rate to be much faster in acid than alkaline medium. In the former, the rate depended largely upon the pH.

Studying the hydrogenation of isoquinoline using a platinum oxide catalyst, Witkop[4] reported a four to one ratio of cis and trans-decahydroisoquinoline when the solvent was acetic acid with a few drops of sulfuric acid. In acetic acid alone, the only isolable product was the cis isomer.

Also significant, is the work of Baker and Schuetz[5] on the high pressure hydrogenation of aromatic compounds using Adams' platinum catalyst. Experiments showed that benzene was not reduced in the absence of solvent or when dissolved in ethanol or dioxane.

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[2] J. Overhoff and J. P. Wibaut, Rec. trav. chim., 50, 957 (1931).

[3] B. Foresti, Boll. Soc. Eustachiana, 38, 19 (1940).

[4] B. Witkop, J. Am. Chem. Soc., 70, 2617 (1948).

R. H. Baker and R. D. Schuetz, J. Am. Chem. Soc., 69, 1250 (1947).

Recently Baker[6] has presented convincing evidence by showing that benzene hydrogenated at low pressures over Adams' catalyst only in the presence of acids. Furthermore, in dioxane solvent and at low concentrations of benzene, the rate was directly proportional to the concentrations of benzene and acetic acid. He postulated a rate-controlling adsorption step, and proposed a transition complex involving a protonated complex of low resonance energy.

4. Catalyst.

Both physical and chemical properties of the catalyst are very important in determining its activity. It is quite difficult to prepare two samples having the same activity and exact procedures must be adhered to if this is attempted. With Adams' platinum catalyst one very important factor is the fusion temperature, which greatly effects the surface area and active centers available for reaction. Finally, trace quantities of materials present either in the solution[7] or in the catalyst surface[8] may alter the activity, this being the well-known action of promotors and inhibitors.

Instead of attempting to prepare identical catalyst samples, a catalyst factor may be calculated which compares the activity of given catalysts to some standard. Subsequently, rate constants may be multiplied by this factor and results are then comparable.

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[6] R.H. Baker, "The Mechanism of the Hydrogenation of Benzene," presented to the American Chemical Society, Chicago, Illinois, September, 1950.

[7] E. F. Cox, Senior Problem, Georgia Institute of Technology, 1949.

[8] R. H. Earle, Jr., "Modifications of Adams' Platinum Catalyst," Master's Thesis, Georgia Institute of Technology, 1950.

C. The Mechanism of Hydrogenation of Aromatic Rings

In spite of the large amount of work on catalytic hydrogenation, the mechanism in unknown. Many theories have been proposed and often these are controversial; none of them explain the facts. Before 1940, it seemed that the intentions were to supplant older pictures, but since then the trend is to apply new facts to the older pictures and ideas. In addition, a mechanism may be valid for a given system while another may be in effect under another set of conditions. A brief summary of the present ideas might be mentioned.

The results of H. A. Smith, et al[9], on the hydrogenation of benzene and its derivatives is explained by an edge-wise adsorption of the phenyl group. There is steric hindrance (1) between the catalyst and adsorbed molecules and (2) of the adsorbed molecule which prevents the approach of hydrogen to the catalyst surface. The latter type could explain the first order dependence on hydrogen pressure, since the rate of adsorption of hydrogen may be the rate-controlling step. The fact that mono-n-alkyl benzenes (excepting toluene) and ϒ-phenyl-n-alkanoic acids have nearly the same rates, fits this picture.

Another interesting contribution of Smith is the determination of the activation energy of the benzene ring. The value of 7,400 calories per mole is much lower than the resonance energy, indicating resonance has been destroyed.

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[9]H. A. Smith, D. M. Alderman, Jr. and F. W. Nadig, J. Am. Chem. Soc., 67, 272 (1945).

It is difficult to comprehend Smith's hypothesis of a monomolecular layer of hydrogen acceptor since it has been shown[10] that the vigorous para-hydrogen conversion takes place in the presence of benzene.

Balandin[11,12] develops a theory on the assumption of two kinds of active centers, one for hydrogen and the other for the hydrogen acceptor. Contrary to Smith, he states that the adsorption equilibrium is much faster than the subsequent reaction. The hydrogenation proceeds through an intermediate partially hydrogenated product.

The results of Herbo[13] showing that cyclohexane retards the hydrogenation of benzene supports the concept of two kinds of active centers. However, he emphasizes that the adsorption of benzene involves physical forces while in the adsorption of hydrogen, chemical valence forces as well as physical forces, are necessary[14]. Over nickel-thoria catalyst the heats of adsorption of benzene is 12,000 calories per mole; for hydrogen, 40,000 calories per mole.

A quantum mechanical treatment is given by Daudel, Pullman, et al.[15-18]

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[10] C. Horrex, R. K. Greenhalgh and M. Polanyi, Trans. Faraday Soc., 35, 511 (1939).

[11] A. A. Balandin, J. Gen. Chem. (U.S.S.R.), 15, 608 (1945).

[12] A. A. Balandin, Bull. acad. sci. U.S.S.R., 1945, 339.

[13] Cl. Herbo, Bull. soc. chim. Belges, 50, 257 (1941).

[14] Cl. Herbo and S. How, Bull. soc. chim. Belges. 52, 135 (1943).

[15] R. Daudel and A. Pullman, Compt. rend., 221, 201 (1945).

[16] R. Daudel and A. Pullman, Compt. rend., 221, 298 (1945).

[17] A. Pullman, Bull. soc. chim. France, 1948, 273.

[18] R. Daudel and C. Sandorfy, Bull. soc. chim. France, 1948, 358.

They interpret the reactivity of organic molecules in terms of electronic charges existing at various positions due to pi electrons. In the case of benzene, two hydrogen atoms are bonded to mobile electrons on the catalyst surface. A benzene molecule is bonded at one of its apexes to the surface between the two hydrogens. The adjacent apex takes on a charge and attaches to the nearest hydrogen. Next, the remaining hydrogen attaches itself to the other apex.

A slightly different view is taken by Rideal[19]. He thought that a catalytic reaction may occur between a gas adsorbed in a primary chemisorbed layer on the catalyst and a second reactant adsorbed above it, either in a van der Waals layer or at gaps in the chemisorbed layer.

Eley[20] believes that the two layer concept is much more probable than the idea of two types of active centers. The latter reaction would require a close balance of two free energies of chemisorption.

In applying the concept of Rideal and Eley to catalytic hydrogenation, several arguments may be made to support this view:

1. Beeck[21] has shown that the energy of activation of the adsorption of hydrogen on metallic surfaces is close to zero. For Adams' platinum-platinum oxide catalyst, this may not be true, but the value is probably small.

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[19]E. K. Rideal, Chemistry and Industry, 62, 335 (1943).

[20]D. D. Eley, Trans. Faraday Soc., 44, 216 (1948).

[21]O. Beeck, Phys. Rev., 17, 61 (1945).

2. It has previously been mentioned that the well-known para-hydrogen conversion takes place in the presence of benzene.[22] This is possible only if the benzene is weakly chemisorbed. Smith's statement that the resonance energy is destroyed is the best evidence for associative adsorption of benzene.

3. Treatment of a platinum catalyst with benzene decreases its activity for hydrogenation to zero; prolonged treatment with hydrogen again increases the activity.[23]

4. The powerful adsorption of hydrogen on metals is due to the partly empty d orbitals which have a much lower energy than the s levels.[24]

To summarize, recent evidence appears to be in favor of a mechanism involving the associative adsorption of the double bond of an aromatic ring followed by reaction with the chemisorbed hydrogen atoms.

It was mentioned in the previous section that catalytic hydrogenation proceeds very slowly with a platinum catalyst unless an acid is present. With pyridine and quinoline, this indicates that the adsorption of these molecules is favored by a low electron density. This is further suggested by the fact that in acid medium pyridine is selectively hydrogenated in the presence of 2-methylpyridine, 2-ethylpyridine and 2-phenylpyridine.[25]

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[22] C. Horrex, R. K. Greenhalgh and M. Polanyi, loc. cit.

[23] A. A. Alchudzhan and A. A. Vvedenskii, J. Gen. Chem. (U.S.S.R.), 16, 415 (1946).

[24] D. D. Eley, Research, 1, 304 (1948).

[25] M. I. Ushakov and M. Sh. Promyslov, J. Gen. Chem. (U.S.S.R.), 17, 1015 (1947).

# III. EXPERIMENTAL

## A. Materials

### 1. Catalyst.

Platinum oxide, prepared by the American Platinum Works, Newark, New Jersey, was used. Catalyst I contained 81.76 per cent platinum; Catalyst II, 81.16 per cent platinum. Several runs were made to determine the relative activity of the two catalysts, since it has been shown[1] that the benzene and pyridine nuclei do not hydrogenate at the same rate and the ratio of these rates may not be constant for different catalyst preparations. Within experimental error, however, catalysts I and II gave the same rate constant for the hydrogenation of both rings.

### 2. Acetic Acid.

Glacial acetic acid was purified by distillation through a 16mm., five-foot helix-packed column with an efficiency of about 40 theoretical plates. The fraction boiling at 116.7 °C. (740 mm.) was collected. Corrected, this value corresponded to a normal boiling point of 118.1 °C.[2]

### 3. Hydrogen.

Hydrogen gas was supplied by the National Cylinder Gas Company, Atlanta, Georgia, and was used without further treatment except filtration through a metal gauze. The pressure of the full tank, approximately 2000 p.s.i., was sufficient for this work.

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[1] A. T. Trimble, Jr., "The Catalytic Hydrogenation of Quinoline," Master's Thesis, Georgia Institute of Technology, 1949, p. 42.

[2] A. Weissberger and E. Proskauer, Organic Solvents (Oxford, Oxford University Press, 1935), p. 43.

4. Quinolines.

Quinoline, 2-methylquinoline, 4-methylquinoline, 6-methylquinoline, 7-methylquinoline and 8-methylquinoline were obtained from Eastman Kodak Company, Rochester, New York, and purified by distillation under nitrogen through an 11 mm., six-foot Vigreaux column having 25 theoretical plates. They were collected at a reflux ratio of ten to one and kept in amber bottles under nitrogen.

The most convenient method for the preparation of 3-methylquinoline[3] is a modification of the Skraup synthesis using α-methylacrolein. In adapting this procedure to this work, nitrobenzene was sulfonated with 20 per cent oleum and the solution diluted with water to a 75 per cent concentration of sulfuric acid. Aniline was dissolved in the mixture and α-methylacrolein[4] slowly added, the reaction temperature being held at 105-110°C. After the addition of the α-methylacrolein was complete, the temperature was raised to 130°C. for 30 minutes. The reaction mixture was cooled, poured onto cracked ice, neutralized with a concentrated solution of sodium hydroxide and steam distilled. The chloroform extract of the steam-volatile products was carefully fractionated, the middle portion of the 3-methylquinoline, boiling point 256.7°C. (740mm.) being used for hydrogenation.

In TABLE I are given the observed boiling points of the quinolines. They have been corrected for stem exposure and to 760 mm. by use of the Clausius-Clapeyron equation, the heats of vaporization being estimated

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[3] W.P. Utermohlen, Jr., J. Org. Chem., 8, 544 (1943).

[4] Supplied by Carbide and Carbon Chemical Division.

from the Kistiakowsky equation.[5]

Hecht[6] compares his values to those given in Heilbron; however, these are actually values taken from Beilstein which are random and a critical evaluation of these has not been made. Jantzen[7] gives the boiling points of all the quinolines and these are listed for comparison; the correlation is better than those listed in Heilbron.

TABLE I

Boiling Points

| Compound | Corrected Boiling Point, °C. | Reported Boiling Point, °C. |
|---|---|---|
| Quinoline | 238.2 | 238.1 |
| 2-Methylquinoline | 248.8 | 247.6 |
| 3-Methylquinoline | 258.6 | 259.6 |
| 4-Methylquinoline | 264.6 | 264.2 |
| 6-Methylquinoline | 258.6 | 258.6 |
| 7-Methylquinoline | 259.2 | 257.6 |
| 8-Methylquinoline | 248.8 | 247.8 |

5. Benzene.

Benzene was purified free from sulfur compounds by washing three

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[5]H. P. Meissner, Ind. Eng. Chem., 33, 1440 (1941).

[6]J. L. Hecht, "The Catalytic Hydrogenation of Quinolines," Master's Thesis, Georgia Institute of Technology, 1950, p. 26.

[7]E. Jantzen, Dechema-Monographie, Berlin, 18, 135 (1932). Values taken from Beilstein's Handbuch der Organischen Chemie, 4th Edition, Volume XX (Berlin, Verlag von Julius Springer, 1935). p. 339.

times with concentrated sulfuric acid, followed by distillation first from metallic sodium and then from Raney nickel. The final product boiled at 80.1 °C. (corrected).

## B. Apparatus

The American Instrument Company, Silver Spring, Maryland, supplied a high-pressure micro shaking mechanism complete with shaker, heating jacket, reaction vessel, valve and gage (Catalogue No. 406-01M).

The shaking mechanism had a heavy cast iron base on which was mounted a one-bearing pedestal for supporting an oscillating trunnion. A heating jacket was clamped to the trunnion and the removable reaction vessel fitted inside the jacket. The gage and valve were mounted directly on the head of the vessel. Agitation was accomplished by a 1/8 horsepower motor mounted on the base. The vessel was rocked through an arc of about 30 degrees at a rate of 34 cycles per minute.

With the switch mounted on the heating jacket in the "low" position, both heating elements were in series to give quarter wattage. The heater was connected to a voltage regulator, thence to a constant voltage box. The temperature was controlled by the regulator and measured by a Weston testing thermometer which fitted through the end of the heating jacket and into the thermowell of the vessel.

A manganese steel reaction vessel with an inside diameter of 3/4 inch and inside depth of six inches was used. The thermowell was bored into the wall of the vessel five inches upwards from the bottom. The compression closure consisted of four parts: (1) the outside cap which screwed on the reaction vessel; (2) thrust bolts; (3) a hardened

steel ring that kept the thrust bolts from marring the pressure head and (4) the inner pressure head with a flat copper gasket. The valve fitted into this inner head and the gage screwed into the valve, completing the assembly. All gas connections were made with superpressure tubing.

A vise was made which held the vessel upright, the grooves in the bottom of the vessel fitting in the vise socket. This device greatly facilitated the removal and reassembly of the cap and head from the vessel.

Pyrex glass liners were necessary in this work to prevent contamination of the hydrogenation mixture. They were made in this laboratory from test tubes without lips. The tubes were first flattened at the bottom with the use of a burner. A small vent-hole midway between the top and bottom of the liner was made to permit equalization of pressure inside and outside, so that the pressure load was carried by the walls of the vessel. A piece of pyrex tubing, having an outside diameter slightly greater than the inside diameter of the liner, was similarly flattened on one end and cut off at the other end, making the length about 3/4 of an inch. With the aid of carborundum grit and oil, a glass-ground joint was made between this top and the liner. It was necessary that a very good fit be made for this joint. About 30 such liners were made.

Since all rate constants had to be corrected for the volume factor, the volume of the bomb with each liner inserted was determined. When the gage volume[8] was added to this value and the volume of materials

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[8] calculated by absolute and pressure-drop methods, 11.7 $\pm$ 0.2 ml.

of the individual run subtracted, the result was the total volume available to hydrogen. This factor was calculated for each run.

## C. Procedure

In each series of experiments conducted here it was desirable to keep all but one variable constant, with the influence of the variable shown in terms of the rate constant.

### 1. Measurement of Materials.

The catalyst was weighed on tared watch glasses by means of an analytical balance and transferred to the hydrogenation liner by use of a camel's-hair brush.

Benzene and acetic acid were measured by pipettes.

All quinoline samples were measured in a device described by Hecht[9] which allowed measurement under nitrogen. A 2 ml. pipette, graduated in hundredths, was used instead of a calibrated tube. The pipette was cleaned, rinsed with methanol and flushed with nitrogen several minutes[10] before taking the sample. This procedure allowed rapid measurement of a sample with an accuracy of two per cent and prevented possible contamination by air oxidation.

### 2. Hydrogenation Technique.

The weighed catalyst was carefully transferred to the liner, followed by addition of the acetic acid. Meanwhile, nitrogen was being passed through the measuring apparatus. The quinoline sample was taken,

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[9] J. L. Hecht, op. cit., p. 28.

[10] A. T. Trimble, Jr., op. cit., p. 27.

added to the acetic acid, the top placed in the liner and the latter carefully lowered into the bomb, always with the vent hole placed in such a position that it would be up when the bomb was placed in the shaker. The reaction vessel was lowered into the table vise and the head assembled. Unless the thrust bolts were screwed in gradually and symmetrically so the head was tight, hydrogen would leak from the bomb. (This fact was observed in some early runs. However, as the groove in the copper gasket became better formed, only a leak of 5 p.s.i. could be detected within one hour. This, of course, was within the experimental error.) The bomb was filled with hydrogen, directly from the cylinder, to the desired pressure. The hydrogen line was disconnected and the bomb placed in the heating jacket, taking care to avoid agitation until normal shaking was started. When a constant temperature was reached (usually about 30 minutes), the shaking mechanism was started. Pressure readings were taken at regular time intervals.

The standard conditions used were as follows: 0.1000 gram catalyst; 0.010 mole of the particular quinoline; 1000 p.s.i. (initial); 4.0 ml. of acetic acid and a temperature of 30.0 $^{o}$C. Each of the factors was varied, but unless otherwise specified, the above values may be inferred.

All glassware used was scrupulously cleaned to avoid possible contamination of the hydrogenation mixture. Each piece was allowed to stand full with sulfuric acid-potassium dichromate cleaning solution; rinsed several times with tap water, then with distilled water; and finally dried in an oven at 110 $^{o}$C. The bomb assembly was cleaned from time to time, the inner parts, before each run. Absorbent cotton and methanol were suitable for cleaning the bomb.

3. Isolation of Products.

Extensive identification of products was not necessary. For most of the substituted quinolines the rate curves followed those observed by other workers, i.e., two first order slopes with a short intermediate stage. The initial slope represented reduction to the 1,2,3,4-tetrahydroquinoline; the second, complete reduction to the decahydroquinoline.

Three runs were made with quinoline using a large liner and bomb having a 256 ± 2 ml. overall gas capacity. These were stopped at a calculated drop of 40 per cent of the theoretical amount of hydrogen. At this point the product should be virtually all tetrahydroquinoline. The hydrogenation mixtures were filtered through a sintered-glass funnel, neutralized with sodium hydroxide and the amines extracted with ether. After removal of the ether in vacuo the amines were distilled through a 7 mm., 15 inch Vigreau column at atmospheric pressure.

The results were very satisfactory. In one experiment, 18 ml. of amines were distilled. GRAPH I shows the results. Fraction I consisted of 1.8 ml. of a clear liquid, boiling point 201.6 °C. ± 0.5 (741 mm.). This corresponded to a normal boiling point of 203.0 ± 0.5 °C. The reported value for trans-decahydroquinoline is 205 °C.[11] Fraction II, 1.9 ml., boiled at 235.8 ± 0.3 °C. (741 mm.); the corrected value is 238.0 ± 0.3 °C. This was considered to be quinoline, boiling point, 238.1 °C.[12] Fraction III, 11.5 ml., boiled at 247.6 ± 0.3 °C. (741 mm.). The corrected value, 250.0 ± 0.3 °C., corresponded to the normal boiling

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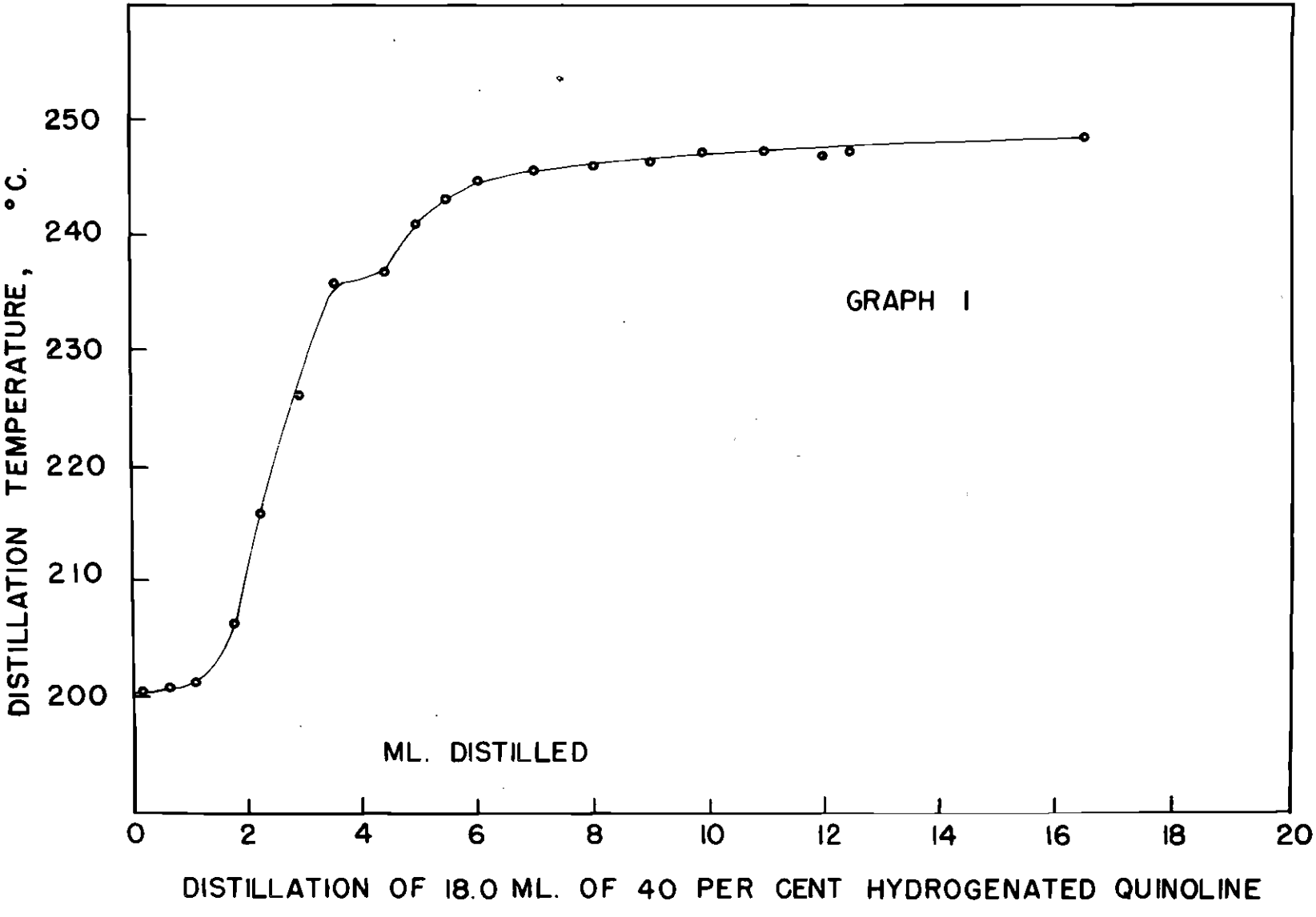
[11] W. Hückel and F. Stept, Ann., 453, 172 (1927).

[12] E. Jantzen, loc. cit.


DISTILLATION TEMPERATURE, °C.
250
240
230
220
210
200
GRAPH I
ML. DISTILLED
0
2
4
6
8
10
12
14
16
18
20
DISTILLATION OF 18.0 ML. OF 40 PER CENT HYDROGENATED QUINOLINE

point of 251 °C.[13] for 1,2,3,4-tetrahydroquinoline. These figures gave an approximate ratio of 7:1:1 for tetrahydroquinoline, quinoline and decahydroquinoline, respectively. These results are explained later.

The rate curves for 2-methylquinoline and 4-methylquinoline did not follow those typical of the other quinolines, i.e., two first order slopes. To determine the cause of these unusual results, hydrogenations were run with these two methylquinolines, stopping them at 40 per cent theoretical pressure drop. For comparison, a similar run was performed with 3-methylquinoline.

The following procedure applies to 2-methylquinoline, 3-methylquinoline and 4-methylquinoline, the purpose being to separate the secondary and tertiary amines. Separate results are given in the following paragraphs.

The hydrogenation product was filtered through a sintered-glass funnel, neutralized with sodium hydroxide and extracted three times with benzene. The benzene was evaporated, leaving only the amine mixture (A).

These amines were added to a benzene solution of benzoyl chloride and refluxed for 30 minutes; the mixture was then poured into dilute hydrochloric acid. A hydrochloric acid layer (I) and a benzene layer (II) were separated.

After (I) was made basic, extracted with benzene and the latter removed by evaporation, only the 5,6,7,8-tetrahydromethylquinoline (Ia) remained (tertiary amine). Refluxing (Ia) with picric acid-ethanol solution gave the picrate (Ib).

Removal of the benzene from (II) gave the crude N-benzoyl derivative of the 1,2,3,4-tetramethylquinoline (IIa) and possibly of the

decahydro analogue. Recrystallization gave (IIb).

TABLE II gives the individual results. They are discussed later.

TABLE II

Products of Hydrogenation[14,15]

| Compound | 2-Methyl-quinoline | 3-Methyl-quinoline | 4-Methyl-quinoline |
|---|---|---|---|
| Initial concentration of acceptor, moles | 0.02 | 0.02 | 0.02 |
| (A), grams product | 2.95 | not isolated | 2.95 |
| (A), per cent yield | 98.8 | ___ | 99.4 |
| (Ia), grams | 0.372 | not isolated | 0.532 |
| (Ia), per cent yield from (A) | 12.7 | ___ | 21.6 |
| (Ib), grams product | 0.303 | 0.119 | 0.454 |
| (Ib), melting point, °C. found | 158 | 167 | 179 |
| (Ib), melting point, °C. reported | 157 | 171 | 170 |
| (Ib), per cent yield from (A) | 4.03 | 1.19 | 6.10 |
| (IIa), grams product | 3.56 | 4.73 | 3.51 |
| (IKa), melting point, °C. found | 113 | 80 | 135 |
| (IKa), melting point, °C. reported | 116 | 84 | 129 |
| (IIa), per cent yield from (A) | 73.2 | 94.9 | 69.4 |
| (IIb), grams product | 2. 21 | not isolated | 2.23 |
| (IIb), melting point, °C. found | 116 | ___ | 136 |
| (IIb), melting point, °C. reported | 116 | | 129 |
| (IIb), per cent yield from (A) | 48.7 | ___ | 45.0 |

[14] all melting points have been corrected.

[15] reported melting points are those of J. von Braun, W. Gmelin and A. Schultheiss, Ber., 56, 1338 (1923).

# IV. DISCUSSION OF RESULTS

## A. Review of Literature

Studies on the hydrogenation of quinoline at low pressures are numerous, with widely varying conditions and many catalysts.[1-6] Moderate conditions or interruption of the reaction lead to the formation of 1,2,3,4-tetrahydroquinoline. With a nickel catalyst, a one per cent yield of the 5,6,7,8-tetrahydroquinoline has been reported[7] along with 71 per cent 1,2,3,4-tetrahydroquinoline. By increasing the temperature[6] or by using a platinum catalyst[5], the decahydroquinoline may be obtained. All workers report exclusively the trans-decahydroquinoline, even at high pressures, except Overhoff and Wibaut.[5] They state that a mixture of the cis and trans forms result when the hydrochloric acid salt of quinoline is hydrogenated in ethanol using Adams' catalyst. It appears unlikely that the less stable cis form is converted to the more stable trans isomer, since two instances[8,9], the cis compound was recovered unchanged on boiling with hydrochloric acid.

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[1] H. Adkins and H. R. Billica, J. Am. Chem. Soc., 70 696 (1948).

[2] G. Darzens, Compt. rend., 149, 1001 (1909).

[3] F. F. Diworky and H. Adkins, J. Am. Chem. Soc., 53, 1868 (1931).

[4] W. Hückel and F. Stepf, Ann., 453, 163 (1927).

[5] J. Overhoff and J. P. Wibaut, Rec. trav. chim., 50, 957 (1931).

[6] P. Sabatier and M. Murat, Compt. rend., 158, 309 (1914).

[7] S. Tsushima and S. Sudzuki, J. Chem. Soc. Japan, 64, 1295 (1943).

[8] V. Prelog and S. Szpilfogel, Helv. Chim. Acta., 28, 1684 (1945).

[9] E. E. King, T. Henshall and R. L. St. D. Whitehead, J. Chem. Soc., 1948, 1373.

Systematic kinetic studies of the hydrogenation of quinoline[10] and methyl quinolines[11] have been made in these laboratories. Using a standard Parr hydrogenation apparatus with a total volume of 4.43 liters, 0.020 moles of acceptor in 50 ml. of acetic acid, 0.1000 grams Adams' catalyst and an initial pressure of 64 p.s.i.; Hecht[11] found the following relative rates of hydrogenation to the tetrahydro form: quinoline, 1.00; 2-methylquinoline, 0.46; 4-methylquinoline, 0.04; 5-methylquinoline, 0.61; 6-methylquinoline, 0.66; 7-methylquinoline, 0.60 and 8-methylquinoline, 1.90. The energy of activation for the reduction of the pyridine ring is 5,800 calories per mole; for the benzene ring, 10,000 calories per mole. All rates were found to be first order in hydrogen pressure, zero order in hydrogen acceptor and directly proportional to the amount of catalyst. It was further observed that the rate of hydrogenation for 2-methylquinoline and 4-methylquinoline decrease rapidly with time. Other factors effecting the rate were investigated.

Quinoline has been reduced at high pressures[12-17] with nickel

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[10] A. T. Trimble, Jr., "The Catalytic Hydrogenation of Quinoline," Master's Thesis, Georgia Institute of Technology, 1949.

[11] J. L. Hecht, "The Catalytic Hydrogenation of Quinolines," Master's Thesis, Georgia Institute of Technology, 1950.

[12] J. von Braun, W. Gmelin and A. Schultheiss, Ber., 56B, 1338 (1923).

[13] F. F. Diworky and H. Adkins, loc. cit.

[14] V. Ipatiev, Ber., 41, 991 (1908).

[15] L. Palfray, Bull. soc. chim. France, 7, 443 (1940).

[16] K. Sugino and J. Mizuguchi, J. Chem. Soc. Japan, 59, 867 (1938).

[17] S. Tsushima and S. Sudzuki, loc. cit.

catalysts, 1,2,3,4-tetrahydroquinoline being the major product. However, trans-decahydroquinoline results on hydrogenation at higher temperature. von Braun, et al[12], studied the hydrogenation of methyl quinolines using a nickel catalyst at 200 °C. and 20 atmospheres hydrogen pressure. Similar to quinoline, 6-methylquinoline, 7-methylquinoline and 8-methylquinoline hydrogenated quantitatively to the 1,2,3,4-tetrahydro derivatives; however, methyl substitution in the pyridine ring caused some 5,6,7,8-tetrahydro product to form simultaneously with the 1,2,3,4-tetrahydromethylquinoline. The following figures are the relative per cent of the 1,2,3,4-tetrahydro and 5,6,7,8-tetrahydro derivatives, respectively, which were obtained; 2-methylquinoline, 96-4; 3-methylquinoline, 66-33; 5-methylquinoline, not studied; 6-methylquinoline, 100-0; 7-methylquinoline, 100-0; and 8-methylquinoline, 100-0.

One case has been reported[18] of the reduction of quinoline at high pressures using a platinum catalyst. The results were only qualitative, the study being one of catalyst fatigue.

At high pressures unrelated cases have been described where Adams' platinum catalyst has been utilized in the reduction of d-primaric acid[19] to the dihydro analogue and in the reduction of L-mannitoic lactone[20] and phenacyl pyridinium bromide[21] to the corresponding hydroxy compounds.

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[18] V. S. Sadikov and A. K. Mikhailov, J. Chem. Soc., 1928, 438.

[19] L. Ruzicka, J. W. Huyser and C. F. Seidel, Rec. trav. chim., 47, 363 (1928).

[20] E. Baer and H. O. L. Fischer, J. Am. Chem. Soc., 61, 761 (1939).

[21] B. Riegel and H. Wittcoll, J. Am. Chem. Soc., 68, 1805, 1913 (1946).

Baker and Schuetz[22] have made the only kinetic study of the reduction of aromatic compounds at high pressures using Adams' platinum catalyst. They found it feasible to reduce benzene and its homologs and phenols on a preparative scale in a matter of minutes, at 1000 to 3000 p.s.i. hydrogen pressure and using glacial acetic acid as a solvent. The kinetics were first order dependence on hydrogen pressure and zero order with respect to the hydrogen acceptor. With napthalene and its derivatives, precise first order rates were observed only after 40 per cent reaction, i.e., after formation of tetralin. Hydrogenation of aniline for 20 hours gave only 17 per cent cyclohexylamine and 22 per cent dicyclohexylamine.

To perfect a technique and to verify the results of Baker, several hydrogenations were made using 0.0226 mole of benzene in 4.0 ml. of glacial acetic acid, 0.064 grams of Adams' catalyst and an initial pressure of 1000 p.s.i. The average rate constant for four identical runs was 0.598 $min.^{-1}$ $gram^{-1}$. Although Baker and Schuetz did not report the actual volume of the hydrogen gas, their bomb was the same size as the one used here, 43 ml., and it seems reasonable to assume the same volume of the system when one considers the pyrex liner. Using the above conditions, they reported a rate constant of 0.60 $min.^{-1}$ $gram^{-1}$. These figures, however, are expected to agree only if the catalysts used were of the same degree of activity. The catalyst used by Baker and Schuetz gave a rate constant of 0.023 $min.^{-1}$ $gram^{-1}$ at 25 °C. for the low pressure hydrogenation of benzene. The catalyst used here gave a rate constant of

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[22] R. H. Baker and R. D. Schuetz, J. Am. Chem. Soc., 69, 1250 (1947).

0.020 $min.^{-1}$ $gram^{-1}$ at 30 °C. for benzoic acid at 64 p.s.i. initial pressure. The k of value for benzene is expected to be about 2.5 times this, or about 0.05. At 25 °C. the latter value would be about 0.04. Such a comparison of catalytic activities does not necessarily hold true at low and high pressures, but since the catalysts used gave rate constants of the same order of magnitude, the results at high pressures are satisfactory.

## B. Nature of the Rate Curve

### 1. Quinoline.

GRAPH II is a first order plot for the hydrogenation of quinoline. Conditions for all runs unless otherwise specified are 1000 p.s.i. initial hydrogen pressure, 0.010 mole of acceptor, 0.1000 gram of catalyst, 4.0 ml. of glacial acetic acid and 30.0 °C. The volume available to hydrogen is approximately 40 ml., all rate constants reported having been corrected by the appropriate factor.

Several interesting facts may be concluded by observation of GRAPH II:

a. Quinoline (0.010 mole) is hydrogenated quantitatively to decahydroquinoline in less than three hours. (This may be accomplished in 30 minutes at 70 °C.)

b. Not apparent from the graph is the rapid initial drop in hydrogen pressure during the first two or three minutes. It is known that the adsorption of hydrogen on the catalyst surface is rapid; and Hecht[23] has shown this to be the case, both in the presence and absence of hydrogen acceptor.

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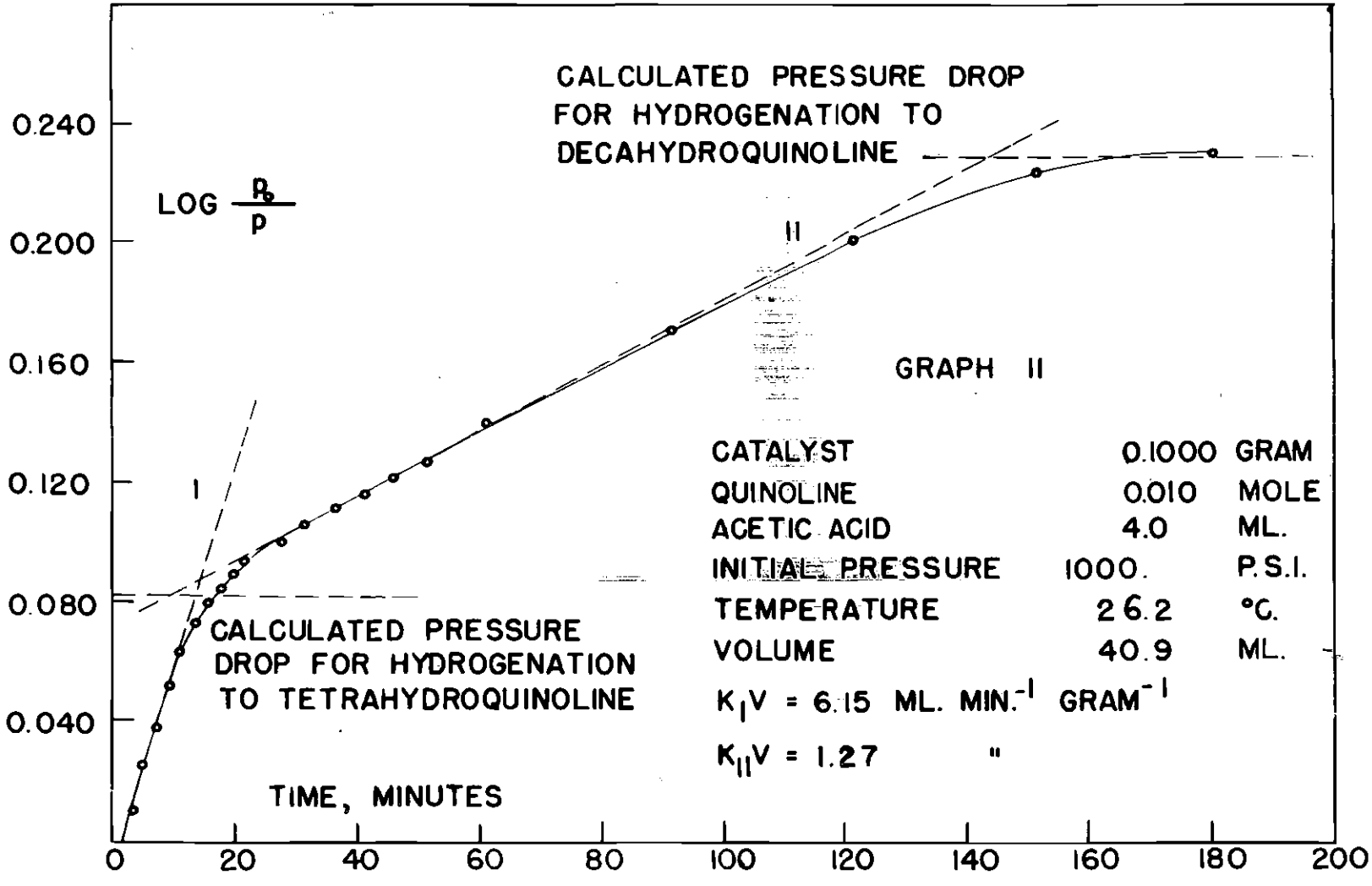
[23] J.L. Hecht, op. cit., pp. 39-40




FIRST ORDER PLOT FOR THE HYDROGENATION OF QUINOLINE

In the present investigation a pressure decrease of approximately 20 p.s.i. in five minutes was observed in each hydrogenation from the time the bomb was placed in the heating jacket, and before shaking was begun. This effect could be due to the adsorption of hydrogen gas, reduction of the platinum oxide catalyst, or diffusion of hydrogen into the solvent. The cooling caused by the expansion of hydrogen gas into the bomb is not a valid explanation, since equilibration to room temperature would increase the pressure.

c. After the rapid initial drop in hydrogen pressure during the first two or three minutes, the curve follows a straight line consistent with first order dependence on hydrogen pressure. The rate constant is 6.15 ml. $min.^{-1}$ $gram^{-1}$; the average value for eight runs is 6.03 ml. $min.^{-1}$ $gram^{-1}$. A more accurate analysis of the curve shows a small, but significant decrease in the slope; the effect being more pronounced as the pressure drop reaches that calculated for complete hydrogenation to a tetrahydroquinoline. This is expected. Obviously the pyridine ring of quinoline is adsorbed preferentially on the catalyst, subsequently forming 1,2,3,4-tetrahydroquinoline; otherwise 5,6,7,8-tetrahydroquinoline would form in noticeable quantities from adsorption and hydrogenation of the benzene ring. The rate of the latter reaction is extremely slow.[24] This selectivity is much more pronounced than the preferential adsorption of the pyridine nucleus of quinoline compared to the benzene ring of 1,2,3,4-tetrahydroquinoline. This is true because the latter two reactions proceed at rates which are the same order of magnitude. The latter reaction, leading to the formation of decahydroquinoline, becomes prominent only

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[24] S. Tsushima and S. Sudzuki, op. cit.

as the concentration of the tetrahydroquinoline increases toward the maximum.

Following the curve to the line calculated for hydrogenation of all the quinoline to the 1,2,3,4-tetrahydroquinoline, it is observed that this does not coincide with the theoretical point for 100 per cent tetrahydroquinoline (intercept of horizontal line with the first slope). This is verified by the data previously mentioned; the experimental concentration ratio of tetrahydroquinoline, quinoline and decahydroquinoline is 7:1:1.

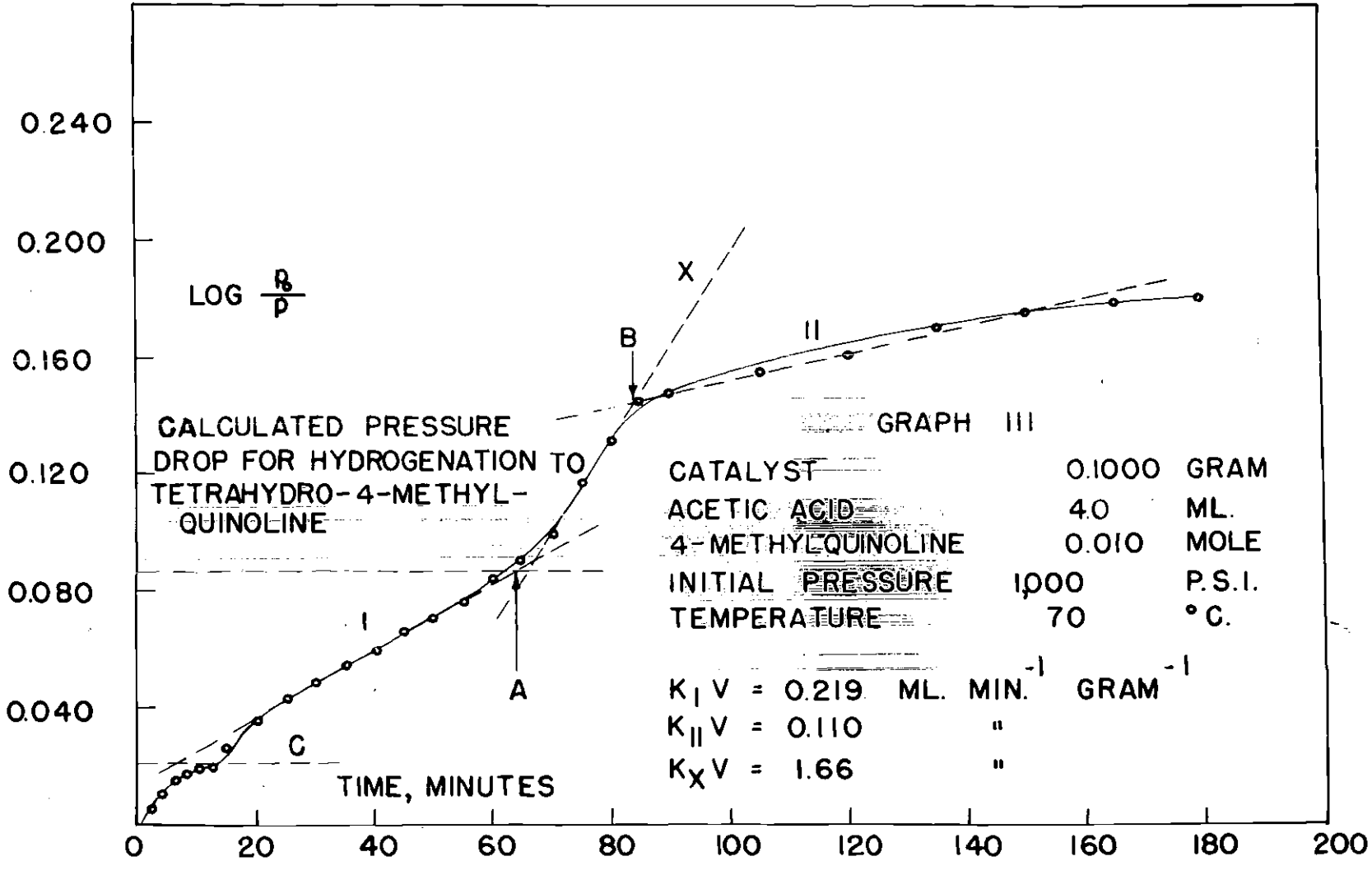
d. Decrease from first order kinetics is larger for the second slope, hydrogenation of tetrahydroquinoline to decahydroquinoline, than for the first slope. As the concentration of hydrogenated product builds up, there is competition for the catalyst surface between species present. It was previously mentioned that errors in the rate expression due to the non-ideality of the hydrogen gas were larger as the ratio of $p_o/p$ became larger. This could account for some of the deviation from first order kinetics for this second slope. Calculation of the rate constant for this step gives 1.27 ml. $min.^{-1}$ $gram^{-1}$; the average value is 1.32.

2. Methylquinolines.

The rate curves for the hydrogenation of 3-methylquinoline, 6-methylquinoline, 7-methylquinoline and 8-methylquinoline are quite similar to quinoline. The rates will be discussed in the next section.

GRAPH III is a first order plot for the hydrogenation of 4-methylquinoline. This run at 70 °C. is reproduced here instead of a run at 30 °C. since the breaks in the curve are more pronounced.

Upon inspection it is apparent that three first order slopes may be drawn instead of two, as with quinoline. Of particular interest is




FIRST ORDER PLOT FOR THE HYDROGENATION OF 4-METHYLQUINOLINE

the very rapid pressure drop, represented by slope X. Also discernable from the graph is the fact that the first and second slopes, I and X, intersect very close to the line representing the fall in pressure equivalent to theoretical complete hydrogenation to a tetrahydro-4-methylquinoline. To clarify this result, runs were stopped at 40 per cent hydrogenation, point A on GRAPH III, and analyses made.

From inspection of TABLE II we may choose the most significant values. The yield of 21.6 per cent of liquid 5,6,7,8-tetrahydro-4-methylquinoline is chosen since recovery of the very soluble picrate is expected to be low. A 69.4 per cent yield of crude 1,2,3,4-tetrahydro-4-methylquinoline is obtained. Any unreacted 4-methylquinoline would be manifest as part of the 21.6 per cent yield, this number representing the total yields of tertiary amines. Similarly decahydro-4-methylquinoline would appear in the larger yield, 69.4 per cent. If the assumption is made that these two compounds are present in approximately equal amounts when the reaction is stopped, as with quinoline, the value 69.4 per cent would be lowered less than 21.6 per cent if corrections for these minor products were made. (The assumption is a 7:1:1 ratio, respectively, of both tetrahydro-4-methylquinolines, 4-methylquinoline and decahydro-4-methylquinoline.) The values taken here are 64 per cent and 14 per cent, respectively, of 1,2,3,4-tetrahydro-4-methylquinoline and 5,6,7,8-tetrahydro-4-methylquinoline. The remaining 23 per cent consists of approximately equal parts of unreacted 4-methylquinoline and decahydro-4-methylquinoline.

von Braun[25] reports 66 per cent and 33 per cent, respectively,

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[25] J. von Braun, loc. cit.

for 1,2,3,4-tetrahydro-4-methylquinoline and 5,6,7,8-tetrahydro-4-methylquinoline, but his method of obtaining these percentages is vague. There is no mention of the possibility of unreacted 4-methylquinoline or completely hydrogenated product. Also, it seems logical to use his figures merely as ratios, not actual yields.

The rapid drop from point A to point B is equivalent to 90 p.s.i. or 0.21 of the total hydrogen required for complete hydrogenation of 4-methylquinoline. It appears entirely reasonable that this drop corresponds to the hydrogenation of the 5,6,7,8-tetrahydro-4-methylquinoline to decahydro-4-methylquinoline, as well as continued hydrogenation of the small amount of 4-methylquinoline still present at point A (about 10 per cent). Calculations reveal that the former reaction would require approximately 40 p.s.i. The fact that the drop is rapid also indicates hydrogenation of the pyridine nucleus.

Examination of slope X shows a decrease in rate like that observed between the first order slopes for quinoline. This effect could easily be simultaneous hydrogenation of the 1,2,3,4-tetrahydro-4-methylquinoline, already present in a large amount. The latter statement is plausible since hydrogenation of the benzene ring is expected to be slow, causing a decrease in rate. This also could account for the remaining 50 p.s.i. pressure drop.

Beyond point B the slope decreases, undoubtedly due to complete reduction of 1,2,3,4-tetrahydro-4-methylquinoline.

One further point of interest of GRAPH III is a small but noticeable dip in the curve after a 45 p.s.i. drop, line C. This represents the addition of 1.0 atoms of hydrogen, however, no attempt at isolation

of products at this point was made.

Hecht[26] states that the hydrogenation of 4-methylquinoline is very slow and decreases rapidly with time. Although he does not mention the fact, his curves show similar breaks. The small change in slope, equivalent to the addition of two atoms of hydrogen, is apparent in several of his runs; but a rapid drop after 40 per cent reaction is noted in only one run. His failure to observe these points is probably because these runs are at low temperature and pressure where the breaks are barely noticeable and because only one run was allowed to react beyond 40 per cent.

GRAPH IV shows a first order plot for the hydrogenation of 2-methylquinoline. Again a run at high temperature, 58.0 °C. is shown so the breaks in the curve are evident. Three changes in slope are apparent, points A, B and C. The first two correspond to the addition of 1.0 and 2.0 atoms of hydrogen, respectively. Although these two breaks do not involve a large change of slope, they are definite and probably significant. The general nature of the entire curve, however, is a steady decrease in the rate with time.

When a run was stopped at 40 per cent reaction, a yield of 72.2 per cent of 1,2,3,4-tetrahydro-2-methylquinoline and 12.7 per cent 5,6,7,8-tetrahydro-2-methylquinoline was obtained (see TABLE II). Corrections similar to those made with 4-methylquinoline would change these to 74 per cent and 6 per cent. von Braun[27] reports 96 per cent and 4 per cent, respectively, the latter number increasing to 35 per cent with substitution of a n-propyl group.

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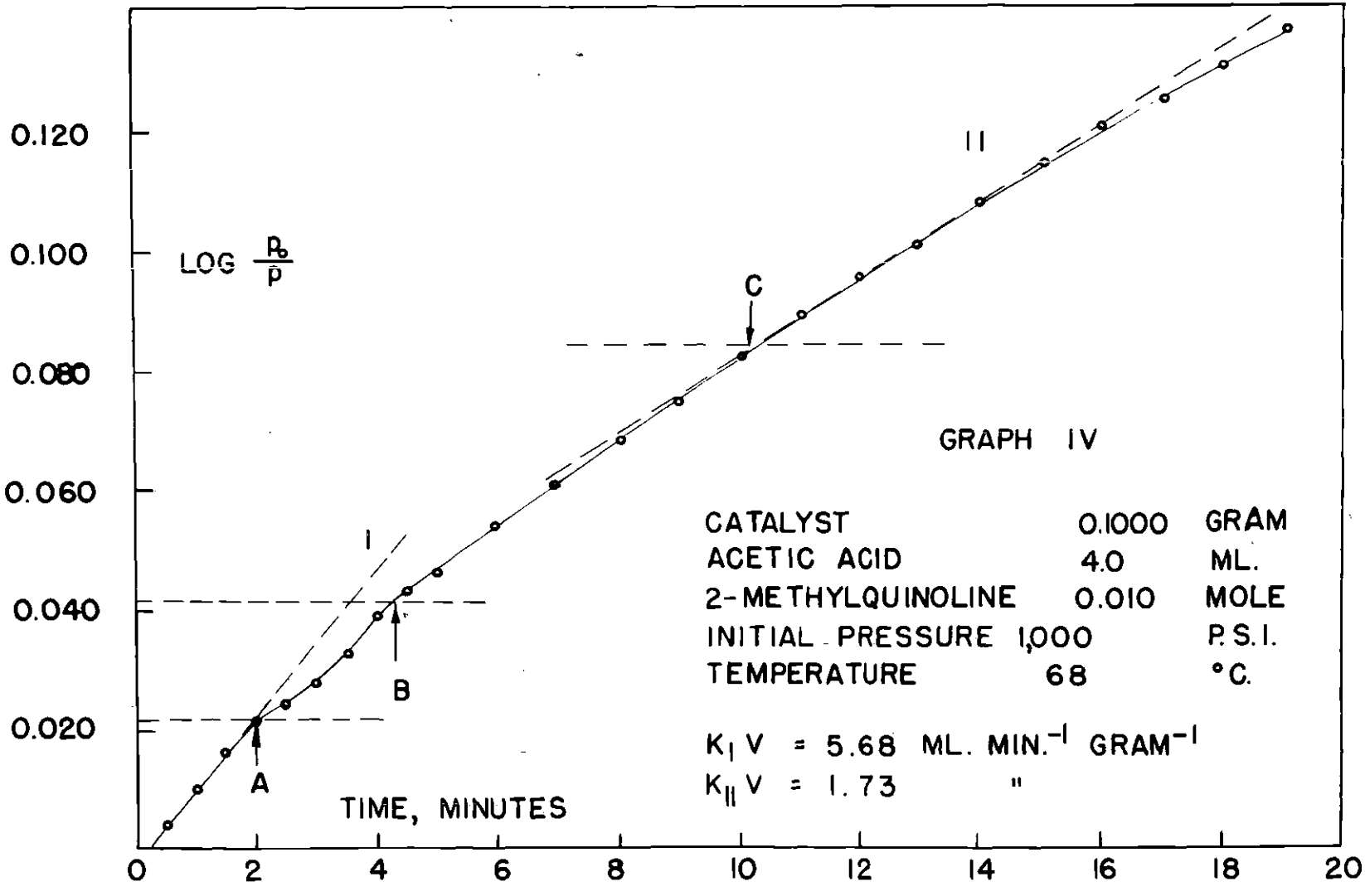
[26] J. L. Hecht, op. cit., p. 41.

[27] J. von Braun, W. Gmelin and A. Petzold, Ber., 57B, 382 (1924).




FIRST ORDER PLOT FOR THE HYDROGENATION OF 2 METHYLQUINOLINE

There is very little change in slope after 40 per cent reaction. However, this is not necessarily because the two tetrahydro-2-methylquinolines hydrogenate at nearly the same rate. In fact, there is very little 5,6,7,8-tetrahydro-2-methylquinoline present and it would not be expected to hydrogenate at the same rate as the 1,2,3,4-tetrahydro-2-methylquinoline; cf., 1,2,3,4-tetrahydro-4-methylquinoline and 5,6,7,8-tetrahydro-4-methylquinoline.

Although the rate curve for the hydrogenation of 3-methylquinoline is similar to quinoline, an analysis was made at 40 per cent reaction. The results are a 95 per cent yield of 1,2,3,4-tetrahydro-3-methylquinoline and a 1.2 per cent yield of 5,6,7,8-tetrahydro-3-methylquinoline. These figures are in agreement with the fact that 40 per cent reaction is equivalent to almost complete hydrogenation of 1,2,3,4-tetrahydro-3-methylquinoline.

C. Effect of Methyl Substitution on the Rate of Hydrogenation

TABLE III shows the effect of methyl substitution on the rate of hydrogenation of quinoline. All rate constants are average values for runs made under the following conditions: 0.1000 gram of catalyst; 0.010 mole hydrogen acceptor; 4.0 ml. of acetic acid; and 1000 p.s.i. initial hydrogen pressure. Each run was corrected to 30.0 $^{o}$C. and one gram of catalyst and multiplied by the volume of the particular system.

It is difficult to correlate structure with reactivity and no attempts will be made here. Obviously several factors are in operation. First, the steric effect of the methyl group is important in the adsorption step on the catalyst. Second, the various resonating structures

of the quinoline must be considered, not forgetting that the quinolinium ion is important in acid medium. It is possible that such structures may be manifest in the adsorption step. However, evidence presented by Smith which indicated that resonance is destroyed when the aromatic ring is adsorbed, suggests that resonating structures have little effect on subsequent reaction after adsorption. The third factor is the inductive or hyperconjugative effect of the methyl group and subsequently the result on the resonance structures.

The rate constants for 3-methylquinoline and 8-methylquinoline are unusually high. Usually methyl substitution lowers the rate of hydrogenation; however Smith has noted that if methyl substitution increases the symmetry of the molecule to which it is added, the rate usually increases.

The rates for 2-methylquinoline, 6-methylquinoline and 7-methylquinoline are approximately equal. Hecht[28] notes a similar comparison and in general his results are comparable. It is probably futile to compare exact rate constants in this case since the conditions, e.g., pressure and concentration, are vastly different.

Of interest is the very slow rate constant for 4-methylquinoline. This has been discussed in the previous section.

Rates of hydrogenation of pyridine, 2-pyridine, 3-methylpyridine and 4-methylpyridine decrease in that order in acid medium and

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[28]J. L. Hecht, op. cit., p. 44.

at low pressures.[29] This is in contrast to the effect observed for quinoline, 2-methylquinoline, 3-methylquinoline and 4-methylquinoline.

TABLE III

Effect of Methyl Substitution on the Rate Constant

| Quinoline | Rate Constant, $k_I V$ ml. $min.^{-1}$ $gram^{-1}$ | Relative Rates (This Work) | Relative[30] Rates (Hecht) | Per Cent Accuracy |
|---|---|---|---|---|
| Quinoline | 6.03 | 1.00 | 1.00 | 3 |
| 2-Methylquinoline | 5.68[31] | 0.94 | 0.46 | 4 |
| 3-Methylquinoline | 8.45 | 1.40 | | 3 |
| 4-Methylquinoline | 0.21[32] | 0.05 | 0.04 | 6 |
| 6-Methylquinoline | 5.22 | 0.87 | 0.60 | 5 |
| 7-Methylquinoline | 5.62 | 0.93 | 0.60 | 3 |
| 8-Methylquinoline | 7.32 | 1.21 | 1.90 | 5 |

TABLE VI shows the effect of methyl substitution on the rate constant for the hydrogenation of 1,2,3,4-tetrahydromethylquinolines. Again the values compare favorably with those of Hecht[33].

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[29] J. A. Stanfield, "Kinetics of Catalytic Hydrogenation," Doctoral Disseration, University of Tennessee, 1947, p. 94.

[30] J. L. Hecht, op. cit., p. 44.

[31] represents slope I, GRAPH IV, p. 37.

[32] represents the slope I, GRAPH III.

[33] J.L. Hecht, loc. cit.

TABLE IV

Effect of Methyl Substitution on the Rate Constant for 1,2,3,4-Tetrahydroquinolines

| Quinoline | Rate Constant, $k_{II}V$ ml. $min.^{-1}$ $gram^{-1}$ | Relative Rates (This Work) | Relative Rates (Hecht)[33] | Per Cent Accuracy |
|---|---|---|---|---|
| Quinoline | 1.32 | 1.00 | 1.00 | 10 |
| 2-Methylquinoline | 1.73 | 1.31 | | 30 |
| 3-Methylquinoline | 1.70[34] | 1.29 | | 30 |
| 4-Methylquinoline | 0.11<br>1.66[35] | 0.08<br>1.26 | | 20<br>30 |
| 6-Methylquinoline | 1.19 | 0.90 | 0.50 | 8 |
| 7-Methylquinoline | 0.83 | 0.63 | 0.28 | 15 |
| 8-Methylquinoline | 0.26 | 0.20 | 0.22 | 15 |

The relative rates of 6-methylquinoline, 7-methylquinoline and 8-methylquinoline are the same order as those listed by Hecht. Notice, however, that the rate constants for 2-methylquinoline, 3-methylquinoline and 4-methylquinoline, the larger value taken for the latter compound, are greater than the rate constant for the hydrogenation of 1,2,3,4-tetrahydroquinoline. These results are not too surprising when it is remembered that at least a part of these rate constants may be attributed to the hydrogenation of the 5,6,7,8-tetrahydromethylquinolines which have been shown to be present in reasonable concentrations.

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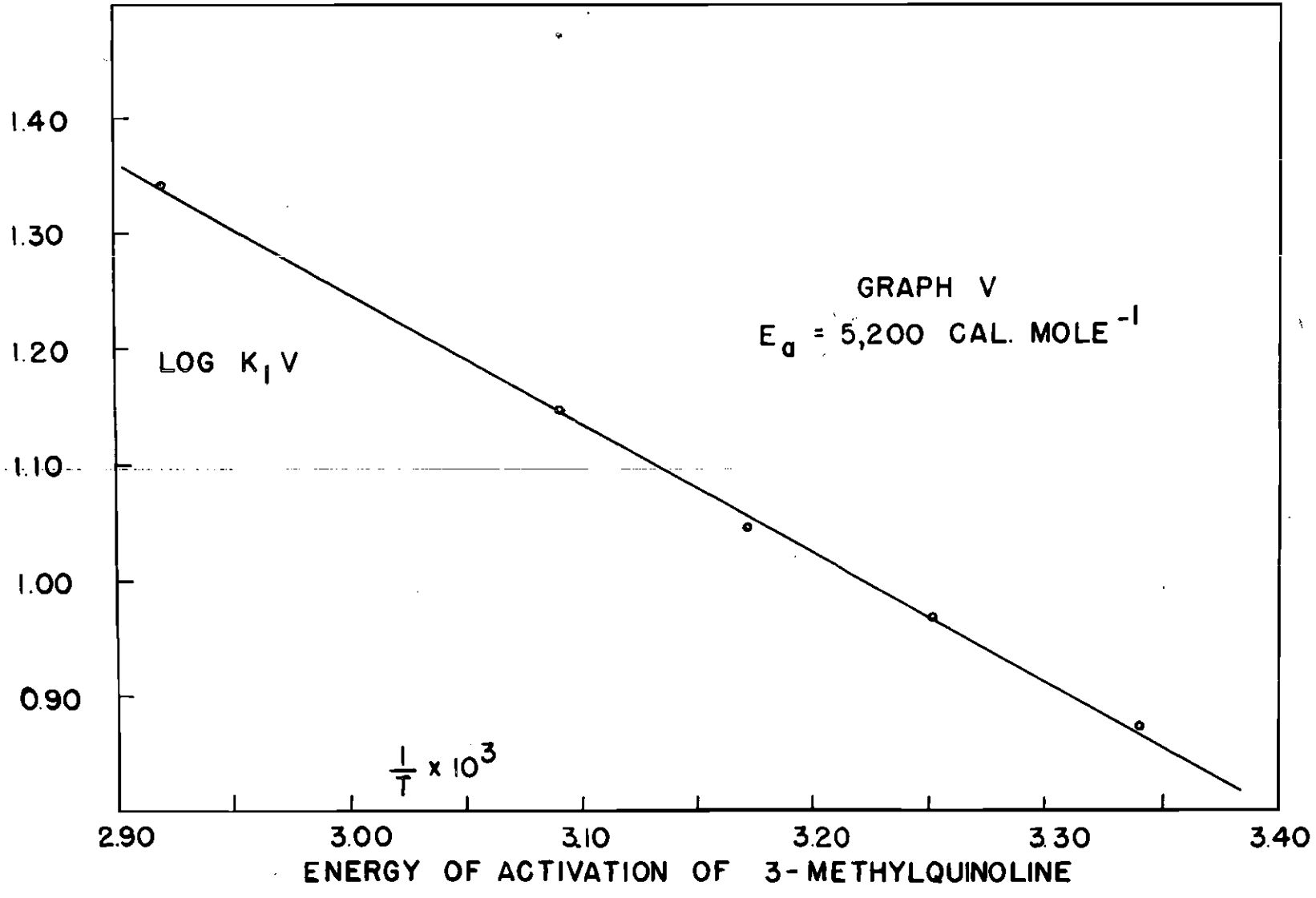
[34] estimated from the energy of activation curve.

[35] represents slope X, GRAPH III, hydrogenation of 5,6,7,8-tetrahydro-4-methylquinoline.

D. Effect of Methyl Substitution on the Energy of Activation

Runs were made with each methylquinoline at temperatures ranging from 20 to 70 °C. in order to determine the activation energies. GRAPH V is a plot of the logarithm of $k_1V$ against the reciprocal of the absolute temperature for 3-methylquinoline. By equation (9), p. 7, the energy of activation is obtained by multiplying the observed slope by -2.30 R. Once the energy of activation is known, a rate constant may be calculated at any other temperature. A frequent use of this is to correct a rate constant at a given temperature to some standard temperature.

TABLE V gives the activation energies for the hydrogenation of the methylquinolines to the tetrahydromethylquinolines. The estimated accuracy is 5 per cent. With 2-methylquinoline, 3-methylquinoline and 4-methylquincline it is likely that the values are actually mixed energies of activation for hydrogenation to the two tetrahydromethylquinolines. The values for hydrogenation of the benzene ring of the 1,2,3,4-tetrahydromethylquinolines to the decahydro analogues are listed in TABLE VI. The latter are only 10 to 20 per cent accurate. Again with 2-methylquinoline, 3-methylquinoline and 4-methylquinoline the energies of activation are mixed because it has been shown that some 5,6,7,8-tetrahydromethylquinolines are present. However with 4-methylquinoline, the two values are given. No conclusions will be made correlating energies of activations with structure. One interesting fact is the low activation energy for the hydrogenation of 5,6,7,8-tetrahydro-4-methylquinoline. The value compares favorably to the hydrogenation of the pyridine rings


1.40
1.30
1.20
1.10
1.00
0.90
LOG $K_1$ V
GRAPH V
$E_a$ = 5,200 CAL. MOLE$^{-1}$
$\frac{1}{T} \times 10^3$
2.90
3.00
3.10
3.20
3.30
3.40
ENERGY OF ACTIVATION OF 3-METHYLQUINOLINE

of the methylquinolines. Hecht[36] reports the activation energy for the reduction of the pyridine ring to be 5,800 calories per mole; the benzene ring, 10,000 calories per mole.

Stanfield[37] finds that the energies of activation of pyridine, 2-methylpyridine, 3-methylpyridine and 4-methylpyridine to vary over the temperature range, 15 to 45 °C. However, from 23 to 45 °C., the average value is 4,500 calories per mole.

TABLE V

Effect of Methyl Substitution on the Energy of Activation for Hydrogenation to the Tetrahydromethylquinolines

| Quinoline | Energy of Activation cal. $mole^{-1}$ |
|---|---|
| Quinoline | 4,500 |
| 2-Methylquinoline | 6,400[38] |
| 3-Methylquinoline | 5,200 |
| 4-Methylquinoline | 8,600[39] |
| 6-Methylquinoline | 3,700 |
| 7-Methylquinoline | 5,100 |
| 8-Methylquinoline | 5,000 |

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[36] J. L. Hecht, op. cit., p. 46.

[37] J. A. Stanfield, op. cit., p. 90.

[38] constant only in the range of 20 to 45 °C.; this figure is for the first rapid drop equivalent to the addition of two atoms of hydrogen, see GRAPH IV.

[39] represents slope I, GRAPH III.

TABLE VI

Effect of Methyl Substitution on the Energy of Activation for the Hydrogenation of Tetrahydromethylquinolines

| Quinoline | Energy of Activation cal. $mole^{-1}$ |
|---|---|
| Quinoline | 9,100 |
| 2-Methylquinoline | 8,700 |
| 3-Methylquinoline | 9,900 |
| 4-Methylquinoline | 7,400<br>5,000[40] |
| 6-Methylquinoline | 7,200 |
| 7-Methylquinoline | 9,600 |
| 8-Methylquinoline | 12,000 |

E. Effect of Variation of Pressure on the Rate Constant

Hydrogenations were made at various pressures to determine the effect on the rate constant, all other variables being held constant. TABLE VII lists the rate constants observed for quinoline and 7 methylquinoline. The values for hydrogenation to the tetrahydroquinolines, $k_I V$, and the decahydroquinolines, $k_{II} V$, are given. Although the change is slight, there is a definite increase in rate with pressure for hydrogenation to the tetrahydroquinoline; and inversely, a decrease in rate for hydrogenation to the decahydroquinolines. The estimated accuracy is 5 per cent.

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[40] represents rapid step X, Graph III, hydrogenation of 5,6,7,8-tetrahydro-4-methylquinoline.

These results are to be compared with those of Baker and Schuetz[41] for the hydrogenation of benzene under similar conditions. They report the rate constant to be independent of the initial pressure over a range of 1000 to 3000 p.s.i.; however, their results appear to be random and are only 15 per cent accurate if their conclusions are true.

TABLE VII

Effect of Pressure on the Rate Constant

| Pressure p.s.i. | Rate Constant, $k_I V$ ml. gram$^{-1}$ min.$^{-1}$ | | Rate Constant, $k_{II} V$ ml. gram$^{-1}$ min.$^{-1}$ | |
|---|---|---|---|---|
| | Quinoline | 7-Methylquinoline | Quinoline | 7-Methylquinoline |
| 500 | | 5.01 | | 1.19 |
| 1,000 | 6.01 | 5.62 | 1.32 | 0.76 |
| 1,500 | 6.54 | 5.90 | 0.75 | 0.63 |
| 2,000 | 6.62 | 6.28 | 0.60 | 0.38 |

F. Effect of Variation of Hydrogen Acceptor

TABLE VIII shows the effect of the variation of the amount of hydrogen acceptor on the rate constant. All runs were made with 4.0 ml. of acetic acid, 30.0 °C., 0.1000 gram catalyst and an initial pressure of 1000 p.s.i. Examination of the second and third columns will show a slight increase in rate while decreasing the amount of the quinolines from 0.010 to 0.005 mole. The other numbers in the second column are equal within experimental error., although the third column shows a slight decrease of rate constant with increasing amount of 8-methylquinoline. These results are expected. As the solution becomes dilute in hydrogen

acceptor there is more catalyst surface available for the rate controling step. There must obviously be a point on the scale where increasing concentration has little or no effect on the initial rate, i.e., the entire catalyst surface is always covered with acceptor. However, the rate curve as a whole would show decreasing first order kinetics because at relatively high concentrations there will be competition between unhydrogenated and hydrogenated species for the catalyst surface. It should be further emphasized that all the solutions in TABLE VIII are actually concentrated. For example, the most dilute quinoline in acetic acid solution is more than one molar.

It would be interesting to center our attention on the other end of the scale. If the concentration of quinoline or 8-methylquinoline was decreased from 0.0050 to 0.0025 mole, we might expect another increase in rate constant. However, some point will be reached where the entire catalyst surface is not covered with acceptor. The consequence is inefficient use of the catalyst, only part of the surface being utilized.

The general nature of a plot of rate constant (ordinate) against the moles of quinoline (abscissa) over a large range would be an increase in rate constant, with increasing concentration, from zero to a maximum, followed by a gradual tapering-off and finally asymptotically approaching a constant value. As the concentration increases to so large a value that the solution is actually a very dilute solution of acetic acid in quinoline, the rate constant should again fall.

The flat constant part of the curve was probably observed by Trimble[42].

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[42] A. T. Trimble, Jr., op. cit., p. 49.

Variation of the amount of quinoline from 0.01 to 0.06 mole in 50 ml. of acetic acid shows no noticeable change in rate. It is reasonable to assume from TABLE VIII that with quinoline, concentrations from 0.010 to 0.030 mole fall within the flat (or constant) part of the curve.

An interesting fact may be seen from the fourth and fifth columns of TABLE VIII. Not only is there an increase of rate with concentration, but the effect is exactly opposite to that in the second and third columns. A similar situation was observed when noting the effect of pressure, i.e., the rate constants for the two hydrogenation steps vary inversely with the given variable. The result is puzzling. Trimble[43] has made similar observations. In addition, he has noted that a given catalyst may give a rate constant, for the hydrogenation of the pyridine ring of quinoline,

TABLE VIII

Effect of Variation of Amount of Quinoline on the Rate Constants

| Quinoline, mole | Rate Constant, $k_I V$ ml. gram$^{-1}$ sec.$^{-1}$ | | Rate Constant, $k_{II} V$ ml. gram$^{-1}$ sec.$^{-1}$ | |
|---|---|---|---|---|
| | Quinoline | 8-Methylquinoline | Quinoline | 8-Methylquinoline |
| 0.005 | 6.61 | 7.90 | 1.21 | 0.111 |
| 0.010 | 5.95 | 7.32 | 1.03 | 0.257 |
| 0.015 | 6.03 | 7.19 | 1.16 | 0.208 |
| 0.020 | 6.00 | 6.58 | 1.77 | 0.372 |
| 0.025 | 5.99 | | 1.67 | |
| 0.030 | 6.07 | | 1.68 | |

[43] A. T. Trimble, Jr., op. cit., p. 43.

greater than a second catalyst; yet the rate constants for the reduction of the benzene ring of tetrahydroquinoline will be in reverse order.

It has been mentioned that deviations from first order kinetics, due to non-ideality of the hydrogen gas, become larger as the pressure drop increases. Since this drop becomes larger as the concentration of the quinoline increases, the results in TABLE VIII are slightly in error.

G. Variation of the Rate Constant with the Amount of Catalyst

Investigations by Smith[44], et al, on the hydrogenation of benzene derivatives reveal that the rate of hydrogenation was first order with respect to hydrogen pressure, zero order with respect to hydrogen acceptor and directly proportional to the amount of catalyst. Trimble[45] and Hecht[46] report the same results with the quinolines. As long as sufficient hydrogen acceptor is present to cover the catalyst surface, one would predict the rate to be directly proportional to the number of "active centers" on the catalyst surface, i.e., the amount of catalyst. Trimble[45] reports a rate constant lower than expected when 0.4000 gram of catalyst are used with 0.020 mole of quinoline in 50 ml. of acetic acid. He states that when the concentration of quinoline is small compared to the amount of catalyst present, there may well be competition for the catalyst surface between quinoline and tetrahydroquinoline. The latter hydrogenates at a much slower rate, consequently a decrease in rate constant is observed. What well may be happening, is incomplete coverage

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[44] H. A. Smith, et al, J. Am. Chem. Soc., 67, 272 (1945), and many later papers.

[45] A. T. Trimble, Jr., op. cit., p. 46.

[46] J. L. Hecht, op. cit., p. 41.

of the catalyst surface with quinoline.

Table IX gives the effect of varying the amount of catalyst on the rate constant. The conditions are 0.010 mole of acceptor in 4.0 ml. of acetic acid at 30.0 °C. Again the situation is complicated because the amount of catalyst, and even acceptor, is very large. With 6-methyl quinoline the rate increases two-fold when varying the amount of catalyst from 0.2000 gram to 0.1000 gram; yet, a decrease to 0.0500 gram increases the rate only about 50 per cent. This may be attributed to fact that we are approaching a concentration where the catalyst has a maximum efficiency.

One further point should be stressed. Although the rate constant per gram catalyst increases by decreasing the amount of catalyst, the rate curve falls off much faster at low amounts of catalyst. This may be attributed to closer competition between the methylquinoline and the 1,2,3,4-tetrahydromethylquinoline for the catalyst when such a small amount of catalyst is present. The latter compound may be desorbed very slowly from the surface, consequently interfering with the adsorption and reaction of the methylquinoline. At higher catalyst amounts, more surface is available to reaction and the rate does not decrease as fast.

TABLE IX

Effect of Amount of Catalyst on the Rate Constant

| Catalyst, gram | Rate Constant, $k_I V$ ml. $gram^{-1}$ $sec.^{-1}$ | |
|---|---|---|
| | 6-Methylquinoline | 7-Methylquinoline |
| 0.0500 | 7.69 | 8.59 |
| 0.1000 | 5.22 | 5.62 |
| 0.2000 | 2.76 | |

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